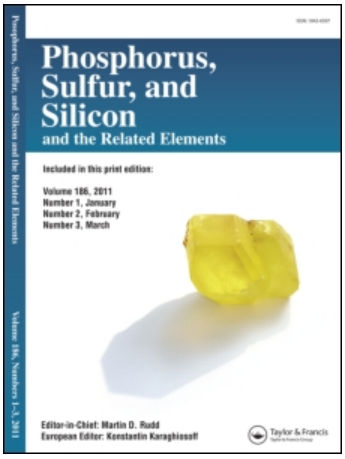

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Synthesis of Mononuclear Cyclopalladated Complexes Containing Tertiary Phosphines (Pph_2et, $P(4\text{-}Mec_6h_4)_3$), Triphenylarsine, Piperidine, Benzylamine, and Pyridine

Seyyed Javad Sabounchei[a]; Kazem Karami[a]
[a] Chemistry Department Science Faculty, Bu-Ali-Sina University, Hamadan, Iran

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Synthesis of Mononuclear Cyclopalladated Complexes Containing Tertiary Phosphines (Pph_2et, $P(4\text{-}Mec_6h_4)_3$), Triphenylarsine, Piperidine, Benzylamine, and Pyridine

Seyyed Javad Sabounchei
Kazem Karami
Chemistry Department Science Faculty, Bu-Ali-Sina University, Hamadan Iran

*When $C_6H_4CH_2NH_2$ and $Pd(OAc)_2$ are reacted in a 1:1 molar ratio in benzene, toluene or acetonitrile at 60–80°C the ortho-metalated complex $[Pd(\mu\text{-}OAc)(C_6H_4CH_2NH_2\text{-}\kappa^2\text{-}C,N)]_2$ (**1**) is obtained. Complex 1 reacts with NaCl or KCl to afford the complex $[Pd(\mu\text{-}Cl)(C_6H_4CH_2NH_2\text{-}\kappa^2\text{-}C,N)]_2$ (**2**). PPh_2Et, $P(p\text{-}tolyl)_3$, $AsPh_3$, piperidine, and pyridine split the chloride bridge in complex 2 to give $[PdCl(C_6H_4CH_2NH_2\text{-}\kappa^2\text{-}C,N)L]$ (L= PPh_2Et (**3a**), $P(p\text{-}tolyl)_3$ (**3b**), $AsPh_3$ (**3c**), piperidine (**3d**), $C_6H_4CH_2NH_2$ (**3e**), pyridine (**3f**)). Complex 3f reacts in THF at room temperature with thallium triflate (TlTfO) and pyridine (molar ratio 1:1:1) to afford complex $[Pd(C_6H_4CH_2NH_2)(py)_2]TfO$ (**4**). Infrared and NMR spectroscopy allow the unambiguous characterization of these products. The molecular structure of $[Pd(C_6H_4CH_2NH_2)(py)_2]TfO$ (**4**) in the crystal was determined.*

Keywords Arsine complexes; cyclopalladation; palladium complexes; pyridine and piperidine complexes; tertiary phoshine complexes

INTRODUCTION

Cyclometallation is receiving much interest in the areas of C—H bond activation and regiochemically controlled organic syntheses.[1–7] Orthopalladation of benzylamines was initially reported by Cope and Friedrich.[8] These authors pointed out that, in order to observe the orthopalladation of these ligands, they should meet the following rules: (a) the benzylamine must be a tertiary amine; (b) the aryl group must not be deactivated with respect to electrophilic substitution, as in 4-nitro-*N*, *N*-dimethylbenzylamine; and (c) the metallacycle formed alter the orthometallation must be a five-membered ring. These rules have been partially broken, however, and it has been proved that

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Address correspondence to Seyyed Javad Sabounchei, Chemistry Department Science Faculty, Bu-Ali-Sina University, Hamadan 65174, Iran. E-mail: jsabouchei@yahoo.co.uk

primary benzylamines can be orthometalated.[6,9–12] Nevertheless, the above work does not change the general situation, and currently the rules of Cope and Friedrich have remained unchanged. In this article, we report the reactivity of the dinuclear complex **2** towards Lewis bases, which produces mononuclear palladium(II) derivatives.

EXPERIMENTAL

Infrared spectra were recorded on Perkin-Elmer 1430 and 16F-PC-FT spectrophotometers in the range of 4000–4200 cm^{-1}, using Nujol mulls between polyethylene sheets. C, H, and N analyses were performed with a Perkin-Elmer 240C microanalyzer. Conductance measurements were carried out in ca. 10^{-4} mol dm^{-3} solutions with a Philips 9501 conductometer and Λ_M is given in Ω^{-1} cm^2mol^{-1}. Melting point were determined with a Reichert apparatus and are uncorrected. NMR spectra were recorded in $CDCl_3$, CD_3COCD_3, CD_2Cl_2 and $(CD_3)_2SO$ with a Varian Unity 300 instrument and a Bruker AC-400 spectrometer. Chemical shifts are referenced to TMS (^1H, ^{13}C) or H_3PO_4 (^{31}P) as external standards.

Reactions were carried out at room temperature without special precautions against moisture. The molar conductivities of all complexes in acetone are between 0–1 $\Omega^{-1}cm^2mol^{-1}$, in agreement with their nonelectrolytic nature, except in complex **4**, for which the molar conductivity is 114 Ω^{-1} cm^2 mol^{-1}, corresponding to its electrolytic nature. Triphenyl-phosphine, tri(*p*-tolyl)phosphine, ethyldiphenylphosphine, triphenylarsine, pyridine, piperidine (Merck, Aldrich), and palladium acetate (Johnson Mattey) were used as received. Palladium(II)acetate was prepared according to the procedure of Stephenson et al.[13]

Single crystals of **4** were investigated by X-ray diffraction. The X-ray intensity data was measured at 100 K an on Bruker SMART APEX CCD-based X-ray diffractometer equipped with a Mo-target X-ray tube ($\lambda = 0.71073$ Å), at the University of Murcia. The detector was placed at a distance of 4.837 cm from the crystal. A total of 1800 frames were collected with a scan width of 0.3° in ω and an exposure time of 10 sec/frame. The frames were integrated with the Bruker SAINT software package,[15] using a narrow-frame integration algorithm. The integration of data was done using a monoclinic unit cell to yield a total of 21623 reflections to a maximum 2θ angle of 53.14° (1.071Å), of which 4062 were independent. Analysis of the data showed negligible decays during data collection. The structure was solved by Paterson method using SHELXS-97,[16] program. The programs use neutral atom scattering factors,$\Delta f'$ and $\Delta f''$ values, and absorption coefficients from ref.[14] The remaining atoms were located via few cycles of least squares

refinements and difference Fourier maps, in the space group P2(1)/c with Z = 4. Hydrogen atoms were input at calculated positions, and allowed to ride on the atoms to which they are attached. Thermal parameters were refined for hydrogen atoms on the phenyl groups using a Ueq = 1.2 Å to precedent atom. The final cycle of refinement was carried out on all non-zero data using SHELXL-97,[17] and anisotropic thermal parameters for all non-hydrogen atoms.

Synthesis of [(Ph_2EtP)PdCl(C_6H_4)CH_2NH_2] (3a)

To a suspension of [Pd(μ-Cl)(C_6H_4)CH_2NH_2]$_2$ (270.5 mg, 0.545 mmol) in dichloromethane (15 mL) at room temperature was added PPh_2Et (0.223 mL, 1.090 mmol). The suspension changed immediately to a clear solution, which was stirred overnight at room temperature. Addition of hexane to the reaction mixture gave the mononuclear triphenylphosphine complex **3a** as a white precipitate, which was filtered off and air dried. ^{1}H NMR ($CDCl_3$, RT): δ 7.86–7.80 (m, 4H, C_6H_5), 7.41–7.26 (m, 6H, C_6H_5), 6.95 (d, $^3J_{HH}$ = 7.2 Hz, 1H, C_6H_4), 6.82 (m, 1H, C_6H_4), 6.47 (t, $^3J_{HH}$ = 6.9 Hz, 2H, C_6H_4), 4.25 (brs, 2H, NH_2), 3.81 (brs, 2H, CH_2), 2.53 (dq, $^2J_{PH}$ = 18.0 Hz, $^3J_{HH}$ = 7.2 Hz,2H, CH_2), 1.14 (dt, $^2J_{PH}$ = 21.6 Hz, $^3J_{HH}$ = 7.2 Hz, 3H, CH_3); ^{31}P NMR ($CDCl_3$, RT): δ36.9; IR (cm^{-1}): ν(N—H) = 3218-3144; M.p.: 181°C; Yield: 417 mg, 0.98 mmol, 89.9%; Λ_M: 1 $\Omega^{-1}cm^2mol^{-1}$ Elemental analysis: Calcd.: C, 54.56; H, 5.02; N, 3.03%; Found: C, 54.54; H, 4.98; N, 3.10%.

Synthesis of [(p-tolyl)$_3$P)PdCl(C_6H_4)CH_2NH_2] (3b)

To a suspension of [Pd(μ-Cl)(C_6H_4)CH_2NH_2]$_2$ (217.5 mg, 0.438 mmol) in dichloromethane (15 mL) at room temperature was added P(p-tolyl)$_3$ (267 mg, 0.876 mmol). The suspension changed immediately to a clear solution, which was stirred overnight at room temperature. Addition of hexane to the reaction mixture gave the mononuclear tri(p-tolyl)phosphine complex **3b** as a white precipitate, which was filtered off and air dried. ^{1}H NMR ($CDCl_3$, RT): δ 7.56 (d, $^3J_{HH}$ = 8.1 Hz, 6H, C_6H_4), 7.12 (d, $^3J_{HH}$ = 6.9 Hz, 6H, C_6H_4), 6.96 (d, $^3J_{HH}$ = 7.2 Hz, 1H, C_6H_4), 6.83 (m, 1H, C_6H_4), 6.41 (m, 2H, C_6H_4), 4.27 (brs, 2H, NH_2), 3.91 (br, 2H, NCH_2); ^{31}P NMR ($CDCl_3$, RT): δ 40.3; IR (cm^{-1}): ν(N—H) = 3252–3198, ν(Pd—Cl) = 275; M.p.: 189°C; Yield: 436 mg, 0.79 mmol, 90.2%; Λ_M: 0.75 $\Omega^{-1}cm^2mol^{-1}$; Elemental analysis: Calcd.: C, 60.68; H, 5.29; N, 2.54%; Found: C, 60.56; H, 5.25; N, 2.57%.

Synthesis of [(Ph_3As)PdCl(C_6H_4)CH_2NH_2] (3c)

To a suspension of [Pd(μ-Cl)(C_6H_4)CH_2NH_2]$_2$ (66.5 mg, 0.134 mmol) in dichloromethane (15 mL) at room temperature was added $AsPh_3$

(76.2 mg, 0.249 mmol). The suspension changed immediately to a clear solution, which was stirred overnight at room temperature. Addition of hexane to the mixture gave the mononuclear triphenylarsine complex 3c as a white precipitate, which was filtered off and air dried. ^{1}H NMR ($CDCl_3$, RT): δ 7.6–7.3 (m, 15H, C_6H_5), 6.95 (d, $^3J_{HH} = 7.2$ Hz, 1H, C_6H_4), 6.84 (d, $^3J_{HH} = 7.2$ Hz, 1H, C_6H_4), 6.42 (m, 2H, C_6H_4), 4.31 (t, $^3J_{HH} = 5.7$ Hz, 2H), 4.14 (br, 2H, NCH_2); IR (cm^{-1}): ν(N—H) = 3252–3198, ν(Pd—Cl) = 275; M.p.: 168°C; Yield: 121 mg, 0.220 mmol, 88.3%; Λ_M: 1 $\Omega^{-1}cm^2mol^{-1}$; Elemental analysis: Calcd.: C, 54.17; H, 4.18; N, 2.53%; Found: C, 53.59; H, 4.02; N, 2.60%.

Synthesis of [(pip)PdCl(C_6H_4)CH_2NH_2] (3d)

To a suspension of [Pd(μ-Cl)(C_6H_4)CH_2NH_2]$_2$ (116.2 mg, 0.234 mmol) in dichloromethane (15 mL) at room temperature was added piperidine (39.8 mg, 0.046.2 mL, 0.468 mmol). The suspension changed immediately to a clear solution, which was stirred overnight at room temperature. Addition of hexane to the reaction mixture gave the mononuclear complex **3d** as a white precipitate, which was filtered off and air dried. ^{1}H NMR ($CDCl_3$, RT): δ 7.00 (m, 3H, C_6H_4), 6.68 (d, $^3J_{HH} = 5.7$ Hz, 1H, C_6H_4), 4.09 (brs, 4H, NCH_2, CH_2-piperidine), 3.05 (br, 4H,NH_2, CH_2-piperidine), 2.53 (br, 1H, NH-piperidine), 1.8 (m, 1H, CH_2-piperidine), 1.59 (br, 1H, CH_2-piperidine), 1.55 (br, 1H, CH_2-piperidine), 1.36 (m, 3H, CH_2-piperidine); IR (cm^{-1}): ν(N—H) = 3336–3324, 3118–3188, ν(Pd—Cl) = 274, 226; M.p.: 185°C (dec); Yield: 163.5 mg, 0.400 mmol, 85.5%; Λ_M: 0 $\Omega^{-1}cm^2mol^{-1}$;Elemental analysis: ($C_{12}H_{19}PdN_2Cl\cdot$ 1/6$CHCl_3$) Calcd.: C, 41.38; H, 5.47; N, 7.90%; Found: C, 41.32; H, 5.12; N, 7.94%.

Synthesis of [($PhCH_2NH_2$PdCl(C_6H_4)CH_2NH_2] (3e)

To a suspension of [Pd(μ-Cl)(C_6H_4)CH_2NH_2]$_2$ (303 mg, 0.61 mmol) in dichloromethane (15 mL) at room temperature was added $PhCH_2NH_2$ (0.134 mL, 1.22 mmol). The suspension changed immediately to a clear solution, which was stirred overnight at room temperature. Addition of hexane to the reaction mixture gave the mononuclear complex **3e** as a white precipitate, which was filtered off and air dried. ^{1}H NMR ($CDCl_3$, RT): δ 7.52–7.27 (m, 5H, C_6H_5), 6.97 (m, 1H, C_6H_4), 6.96 (d, $^3J_{HH} = 5.2$ Hz, 2H, C_6H_4), 6.80 (t, $^3J_{HH} = 4.0$ Hz, 1H, C_6H_4), 4.90 (brs, 2H, NH_2), 4.07 (m, 2H, CH_2), 3.99 (m, 2H, NH_2), 3.83 (t, $^3J_{HH} = 6.0$ Hz, 2H, CH_2); IR (cm^{-1}): ν(N—H) = 3268-3208, 3116-3052, ν(Pd—Cl) = 346, ν(Pd—C) = 236, ν(Pd—N) = 264, 288; M.p.: 178°C (dec); Yield: 404 mg, 0.95 mmol, 77.9%; Λ_M: 0.5 $\Omega^{-1}cm^2mol^{-1}$.

Synthesis of [(py)PdCl(C_6H_4)CH_2NH_2] (3f)

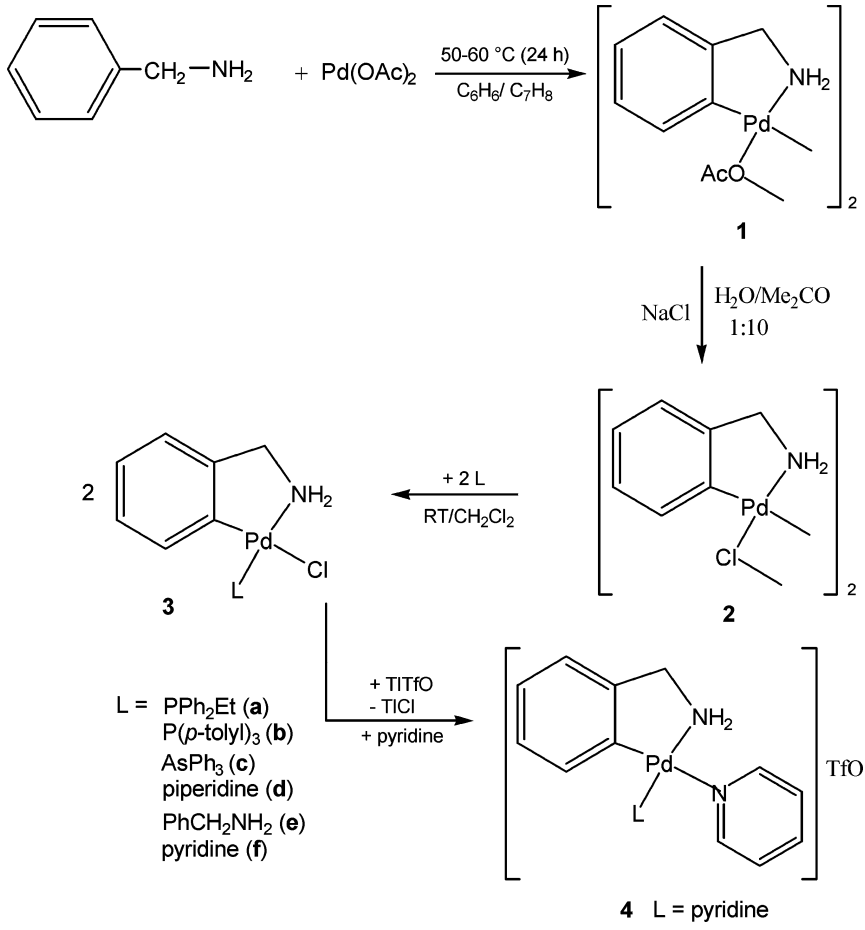
To a suspension of [Pd(μ-Cl)(C_6H_4)CH_2NH_2]$_2$ (292 mg, 0.588 mmol) in dichloromethane (15 mL) at room temperature was added pyridine (0.095 mL, 1.176 mmol). The suspension changed immediately to a clear solution, which was stirred overnight at room temperature. Addition of hexane to the reaction mixture gave the mononuclear pyridine complex **3f** as a white precipitate, which was filtered off and air dried. ^{1}H NMR ($CDCl_3$, RT): δ 8.49 (d, $^3J_{HH}$ = 6.0 Hz, 2H, pyridine-H), 7.63 (t, $^3J_{HH}$ = 6.0 Hz, 1H, pyridine-H), 7.04 (m, 4H, pyridine-H, C_6H_4), 6.83 (t, $^3J_{HH}$ = 6.0 Hz, 1H, C_6H_4), 6.08 (d, $^3J_{HH}$ = 9.0 Hz, 1H, C_6H_4), 4.66 (brs, 2H, NH_2), 4.20 (t, $^3J_{HH}$ = 6.0 Hz, 2H, CH_2); IR (cm^{-1}): ν(N—H) = 3300-3200, ν(C=N py) = 1620; M.p.: 183°C (dec); Yield: 327 mg, 1 mmol, 85%; Λ_M: 0 $\Omega^{-1}cm^2mol^{-1}$; Elemental analysis: Calcd.: C, 44.06; H, 4.01; N, 8.58%; Found: C, 43.59; H, 3.75; N, 8.50%.

Synthesis of [(py)$_2$Pd(C_6H_4)CH_2NH_2]TfO (4)

To a solution of [(py)PdCl(C_6H_4)CH_2NH_2] **3f** (33.8 mg, 0.100 mmol) in CH_2Cl_2 (10 mL) TlTfO (35.5 mg, 0.100 mmol) was added. The resulting suspension was stirred for 1 h at room temperature and filtered through a plug of celit or $MgSO_4$. To the freshly obtained solution, cooled at 0°C, pyridine (8 μL, 0.100 mmol) was added. After of stirring for 1 h at 0°C,the crude complex **4** precipitated as a pale yellow solid. The solvent was removed and addition of hexane to the crude product yielded complex **4** as a yellow powder, which was filtered off, washed with cold Et_2O and air dried. Complex **4** is soluble in CH_2Cl_2, $CHCl_3$, acetone, and *n*-hexane. Crystalline yellow prisms of **4** were grown by slow diffusion from a CH_2Cl_2/*n*-hexane solvent system; ^{1}H NMR (acetone-d_6, RT): δ 9.04 (d, $^3J_{HH}$ = 7.2 Hz, 2H, pyridine-H), 8.78 (d, $^3J_{HH}$ = 7.8 Hz, 2H, pyridine-H), 8.01 (tt, $^3J_{HH}$ = 7.8 Hz, $^5J_{HH}$ = 1.5 Hz, 1H, pyridine-H), 7.97 (tt, $^3J_{HH}$ = 7.8 Hz, $^5J_{HH}$ = 1.5 Hz, 1H, pyridine-H), 7.66 (td, $^3J_{HH}$ = 7.2 Hz, $^5J_{HH}$ = 1.5 Hz, 2H, pyridine-H), 7.59 (td, $^3J_{HH}$ = 7.2 Hz, $^5J_{HH}$ = 1.2 Hz, 2H, pyridine-H), 6.95 (d, $^3J_{HH}$ = 6.9 Hz, 2H, C_6H_4), 6.74 (t, $^3J_{HH}$ = 7.8 Hz, 1H, C_6H_4), 5.99 (dd, $^3J_{HH}$ = 7.8 Hz,$^5J_{HH}$ = 0.9 Hz, 1H, C_6H_4), 5.25 (br, 2H, NH_2), 4.28 (t, $^3J_{HH}$ = 6.0 Hz, 2H, NCH_2); IR (cm^{-1}): ν(N—H) = 3252-3198, ν(C=N py) = 1620, 1624; M.p.: 176°C; Yield: 42 mg, 0.079 mmol, 79%; Λ_M: 114 $\Omega^{-1}cm^2mol^{-1}$ Elemental analysis: Calcd.: C, 41.59; H, 3.49; N, 8.08; S, 6.17%; Found: C, 41.20; H, 3.37; N, 8.12; S, 6.09%.

RESULTS AND DISCUSSION

When benzyl amine was reacted with $Pd(OAc)_2$ (molar ratio 1:1) in acetone at room temperature, the complexe **1** was isolated. We propose for this reaction the same mechanism, which was previously reported for primary benzylamines.[12] Complex **1** reacts with NaCl to afford the dinuclear complexe 2, where the bridging acetate groups has been substituted by chloride anions. The chloro-bridged dimer undergoes bridge-splitting reactions with piperidine, ethyldiphenylphosphine, tris(*p*-tolyl)phosphine, triphenylarsine, and benzylamine affording the corresponding mononuclear cyclopalladated complexes **3** (Scheme 1). Treatment of a solution of 3f in THFwith TIOTF and pyridine allowed the isolation of the ionic mononuclear complex **4** (Scheme 1).



SCHEME 1

In the ^{1}H NMR spectra of the mononuclear complexes **3** and **4** the chemical shift of the NH_2 group of benzylamine was shifted to low field compared to that of free benzylamine, which is consistent with its coordination to palladium. Furthermore, the NMR signals of four different aromatic protons originating from the benzyl amine moiety were clearly detected in the region between 6 and 7 ppm. In addition, the NMR signal of proton H-6 in compounds **3f** and **4** appears as doublet at 6.08 and at 5.99 ppm, respectively, confirming the orthopalladated structure.[12,18] These results showed that the cyclopalladation occurred definitely at the sp^2 carbon atom of the benzyl group. This is in agreement with the general finding, that examples of C—H bond activation are much more numerous for aromatic than for aliphatic C—H groups. As pointed out by Raybov[19] as well as by Lavin et al.,[20] a reasonable explanation is that even in cyclopalladation reactions by palladium acetate, an initial C—H bond interaction with the metal center is essential for the following metallation step; an aromatic ring can interact more easily with palladium metal in an η^2-fashion than an alkyl C—H bond, through an agostic interaction. In the mononuclear complexes **3**, derived from benzyl amine, the methylene protons were observed as triplets due to coupling with the adjacent NH_2 protons, while the NH_2 protons gave only one broad signal. The ^{31}P NMR spectrum of compounds **3a** and **3b** shows a singlet at 36.9 and 40.3 ppm, respectively, confirming that these compounds consisted of only one isomer in which the amino group and the phosphine ligand are located *trans* to each other; demonstrating once again the well-established tendency of PPh_2Et, P(*p*-Tolyl)$_3$ and aryl ligands avoid a trans orientation to each other when coordinated to palladium (Scheme 1). We propose for this destabilizing effect between pairs of trans ligands in palladium complexes the term of *transphobia*. This term has also been used by other authors.[21] In the IR spectra a decrease of ν(N—H) for the mononuclear and dinuclear complexes indicated the coordination of NH_2 to palladium.

Crystal and Molecular Structure of $[(Py)_2Pd(C_6H_4)CH_2NH_2]$ TfO (4)

Single crystals of $[(py)_2Pd(C_6H_4)CH_2NH_2]$TfO (**4**), suitable for X-ray diffraction were obtained from a CH_2Cl_2/*n*-hexane solvent system. The details of structure determination are given in Table I, bond lengths and angles are presented in Table II, details on the hydrogen bonds are contained in Table III. A thermal ellipsoid ORTEP[25] drawing of **4** with atomic number scheme of the obtained structure is presented in

TABLE I Crystal Data and Structure Refinement for Complex 4

Empirical formula	$C_{18}H_{18}F_3N_3O_3PPdS$
Formula weight	519.81
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 11.6056(5) Å $\alpha = 90^\circ$ b = 17.9538(8) Å $\beta = 97.256(2)^\circ$ c = 9.6180(4) Å $\gamma = 90^\circ$
Volume	1988.00(15) $Å^3$
Z	4
Density (calculated)	1.737 g/cm^3
Absorption coefficient	1.091 mm^{-1}
F (000)	1040
Crystal size	0.27 × 0.12 × 0.12 mm
Theta range for data collection	1.77 to 26.37°
Index ranges	$-14 \le h \le 14$, $-22 \le k \le 22$, $-12 \le l \le 12$
Reflections collected	21623
Independent reflections	4062 [R(int) = 0.0202]
Completeness to theta = 26.00°	100.0%
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8802 and 0.7572
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4062 / 7 / 270
Goodness-of-fit on F^2	1.071
Final R indices [I > 2sigma (I)]	R1 = 0.0211, wR2 = 0.0525
R indices (all data)	R1 = 0.0226, wR2 = 0.0534
Largest diff. peak and hole	0.533 and -0.323 e.$Å^{-3}$

Figure 1. In the complex **4** the palladium atom shows a slightly distorted square planar environment with angles of 177.77(6)° and 176.29(7)° for N(1)-Pd(1)-N(3) and C(1)-Pd(1)-N(2), respectively. The benzylamine moiety acts as a chelate ligand forming a fivemembered ring Pd(1)-N (3)-C (7)-C (2)-C(1). This ring is quite strained as indicated by the angles N(1)-Pd(1)-N(2) 93.70(6)°, C(1)-Pd(1)-N(3) 95.07(7)°, C(1)-Pd(1)-N(1) 82.71(7)° and N(3)-Pd(1)-N(2) 88.52(6)°. The distances Pd(1)-N(3) of 2.039(1) Å and Pd(1)-(N(3) of 2.042(1) Å are similar to those found in analogous complexes,[22,23] and the Pd(1)-N(2) distance to the nitrogen atom of the pyridine ring also falls in the usual range of distances found for this type of complexes.[20,24] The Pd(1)-N(2) distance (2.131(1) Å) is larger than the Pd(1)-N(1) and Pd(1)-N(3) distances, since the nitrogen

TABLE II Bond Lengths [Å] and Angles [°] for Complex 4

TBPd(1)-C(1)	1.9881(18)	C(24)-C(25)	1.380(3)
Pd(1)-N(1)	2.0388(15)	C(99)-F(2)	1.320(2)
Pd(1)-N(3)	2.0419(15)	C(99)-F(1)	1.325(3)
Pd(1)-N(2)	2.1307(16)	C(99)-F(3)	1.340(2)
N(1)-C(7)	1.487(2)	C(99)-S(1)	1.826(2)
N(2)-C(11)	1.342(2)	S(1)-O(3)	1.4355(14)
N(2)-C(15)	1.347(2)	S(1)-O(1)	1.4368(15)
N(3)-C(25)	1.342(2)	S(1)-O(2)	1.4469(15)
N(3)-C(21)	1.345(2)	C(1)-Pd(1)-N(1)	82.71(7)
C(1)-C(6)	1.395(3)	C(1)-Pd(1)-N(3)	95.07(7)
C(1)-C(2)	1.415(3)	N(1)-Pd(1)-N(3)	177.77(6)
C(2)-C(3)	1.391(3)	C(1)-Pd(1)-N(2)	176.29(7)
C(2)-C(7)	1.498(3)	N(1)-Pd(1)-N(2)	93.70(6)
C(3)-C(4)	1.386(3)	N(3)-Pd(1)-N(2)	88.52(6)
C(4)-C(5)	1.387(3)	C(7)-N(1)-Pd(1)	111.43(12)
C(5)-C(6)	1.390(3)	C(11)-N(2)-C(15)	118.20(16)
C(11)-C(12)	1.385(3)	C(11)-N(2)-Pd(1)	121.31(12)
C(12)-C(13)	1.387(3)	C(15)-N(2)-Pd(1)	120.42(12)
C(13)-C(14)	1.382(3)	C(25)-N(3)-C(21)	118.13(16)
C(14)-C(15)	1.380(3)	C(25)-N(3)-Pd(1)	119.43(12)
C(21)-C(22)	1.375(3)	C(21)-N(3)-Pd(1)	122.29(12)
C(22)-C(23)	1.375(3)	C(6)-C(1)-C(2)	117.91(17)
C(23)-C(24)	1.382(3)	C(15)-C(14)-C(13)	118.72(18)
C(6)-C(1)-Pd(1)	128.49(14)	N(2)-C(15)-C(14)	122.71(18)
C(2)-C(1)-Pd(1)	113.58(14)	N(3)-C(21)-C(22)	122.37(18)
C(3)-C(2)-C(1)	120.44(17)	C(23)-C(22)-C(21)	119.48(18)
C(3)-C(2)-C(7)	122.57(17)	C(22)-C(23)-C(24)	118.49(18)
C(1)-C(2)-C(7)	116.89(16)	C(25)-C(24)-C(23)	119.35(19)
C(4)-C(3)-C(2)	120.65(18)	N(3)-C(25)-C(24)	122.17(18)
C(3)-C(4)-C(5)	119.38(19)	F(2)-C(99)-F(1)	108.77(17)
C(4)-C(5)-C(6)	120.54(18)	F(2)-C(99)-F(3)	107.16(18)
C(5)-C(6)-C(1)	121.04(17)	F(1)-C(99)-F(3)	107.43(17)
N(1)-C(7)-C(2)	108.75(15)	F(2)-C(99)-S(1)	111.44(14)
N(2)-C(11)-C(12)	122.44(17)	F(1)-C(99)-S(1)	111.37(15)
C(11)-C(12)-C(13)	118.77(18)	F(3)-C(99)-S(1)	110.50(14)
C(14)-C(13)-C(12)	119.15(18)	O(3)-S(1)-O(1)	115.75(9)
		O(3)-S(1)-O(2)	115.44(9)
		O(1)-S(1)-O(2)	113.28(10)
		O(3)-S(1)-C(99)	103.77(9)
		O(1)-S(1)-C(99)	103.54(9)
		O(2)-S(1)-C(99)	102.78(9)

atom N(3) is located trans to the Pd—C σ-bond, which displays a large trans influence. Finally, it should be noted, that a N—H$\cdots$O hydrogen bond is observed between the cationic complex and the triflate anion (Table III).

TABLE III Parameters of Hydrogen Bonds [Å and °] for Complex 4

D—H. . .A	d(D—H)	d(H. . .A)	d(D. . .A)	<(DHA)
N(1)-H(01A)· · ·O(1)[a)]	0.854(18)	2.355(19)	3.181(2)	163(2)
N(1)-H(01A)· · ·O(2)[a)]	0.854(18)	2.65(2)	3.287(2)	132.7(19)
N(1)-H(01B)· · ·O(2)[b)]	0.850(18)	2.095(19)	2.927(2)	166(2)
C(7)-H(7A)· · ·Pd(1)[c)]	0.99	3.09	4.038(2)	160.9
C(13)-H(13)· · ·O(2)[d)]	0.95	2.50	3.413(2)	161.3
C(14)-H(14)· · ·O(1)[e)]	0.95	2.34	3.248(2)	159.4

Symmetry transformations used to generate equivalent atoms: [a)] −x+1, −y+1, -z+1; [b)] −x+1, y-1/2, −z+3/2; [c)] x, −y+1/2, z-1/2; [d)] x, −y+3/2, z+1/2; and [e)] x, y, z+1.

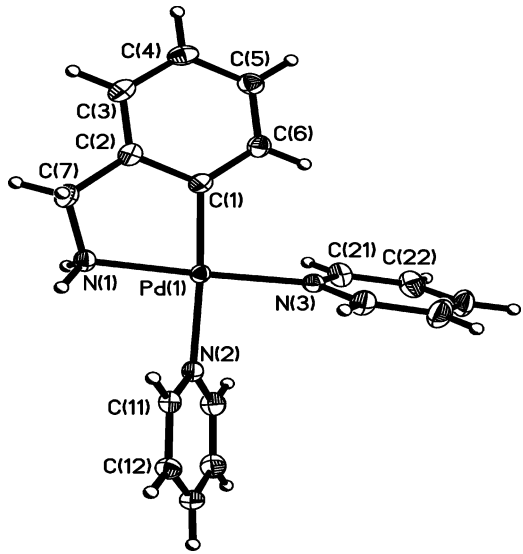


FIGURE 1 Molecular structure of complex 4 in the crystal; ORTEP plot showing the labeling scheme; thermal ellipsoid are drawn at the 50% probability level.

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